Microstructure Analysis and Optimization of Sputter-Deposited Zinc Oxide Thin Films Used in Low-Emissivity Coatings for Energy Efficient Windows

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ZnO thin films were deposited with changing oxygen gas pressure and their microstructures were investigated by the glancing incident X-ray reflectivity measurement. It was found that the ZnO thin films exhibited higher packing density and smoother surface morphology, when they were deposited in lower oxygen gas pressure. These microstructure improvements of ZnO thin films with decreasing in oxygen gas pressure should come from the increase in the kinetic energy of sputtered Zn atoms and gas particles such as oxygen negative ions recoiled from the sputtering target surface. Furthermore, the double-layered low-emissivity coatings consisting of glass/ZnO/Ag were also prepared and the correlation between the microstructure of ZnO thin films and the electrical property of the Ag thin films was clarified. The Ag thin films exhibited low electrical resistivity when the ZnO thin films deposited in low oxygen gas pressure were used. It can be considered that this improvement in the Ag resistivity is attribute to the high packing density and smooth surface of the ZnO thin film.

Key words: Ag, low-emissivity coating, packing density, sputtering, ZnO

1. INTRODUCTION

Insulating glass units constructed of a pair of glass panes are used as energy efficient windows for buildings. Besides, low-emissivity (low-e) coatings are often deposited on one side of the glass panes by magnetron sputtering to improve thermal emission and solar reflectance toward outside room [1,2]. Since Ag exhibits lowest electrical resistivity and emissivity in infrared light among of all metals, the low-e coatings are usually consisting of the Ag-based multilayer, such as glass/under-dielectric/Ag/over-dielectric or the repetition structure, moreover, ZnO-based thin films are often used as the dielectrics. Nowadays, the low-e coatings are required to exhibit not only high solar energy reflectance but also high visible light transmittance. However, the low-e coating which exhibits both performances has not been available yet, because the Ag thin films used in low-e coatings exhibit much higher resistivity than the bulk Ag; therefore, that leads to a decrease in solar reflectance per unit Ag thickness [3]. It has been reported that the sputtering deposition conditions for Ag thin films, such as cathode voltage [4], pulse frequency applied to sputtering target [5], substrate bias voltage [6], gas pressure [7] and gas component [8,9], influence the resistivity of Ag thin films. Moreover, previous studies have revealed that the resistivity of the Ag thin films used in the low-e coatings strongly depends on the microstructures and compounds of

under-dielectrics such as ZnO, Al-doped ZnO and SnO_2 [10-12]. However, the optimum microstructures of under-dielectrics to obtain low-resistive Ag thin film used in low-e coatings have not fully been clarified yet. In this paper, we present the microstructures of ZnO thin films as a function of oxygen gas pressure during the sputtering deposition. Besides, the correlation between oxygen gas pressure and microstructures of the ZnO thin films is discussed. Furthermore, double-layered low-e coatings such as glass/ZnO/Ag were prepared using the ZnO under layers deposited in various oxygen gas pressure. Here, the over-dielectrics were not coated on the Ag layers in order to avoid the complication. Then, the optimum microstructures of ZnO under layers used in low-e coatings are suggested on the basis of the microstructure analysis.

2. EXPERIMENTAL

All thin films were deposited on soda-lime-silicate glass substrates at room temperature by dc magnetron sputtering. ZnO single layers with the thickness of about 125 nm were deposited using a Zn pure metal target; the applied power was 100 W; oxygen gas pressure was varied from 0.2 to 3.0 Pa. Low-e coatings with a layer construction of glass/ZnO/Ag were deposited; the deposition conditions of ZnO under layers correspond to those of ZnO single layers. The 10-nm-thick Ag thin films were deposited

with 0.5 Pa argon gas and pure Ag target; the applied power was 50 W. Each layer with the designed thickness in the low-e coatings was deposited adjusting the deposition time.

X-ray diffraction (XRD, using CuK α radiation) measurement with out-of-plane arrangement was carried out to evaluate the crystal structure of ZnO thin films. Glancing incident X-ray reflectivity (GIXR) measurement was performed to evaluate the packing density and surface roughness (Rms) of the ZnO thin films [13]. The relative packing density (RPD) was calculated using the following equation:

$$\text{RPD} = \frac{\text{Measured packing density (g/cm}^3\text{)}}{\text{Maximum packing density (g/cm}^3\text{)}}, \quad (1)$$

where the maximum packing density means maximum value estimated in the GIXR measurement for ZnO thin films. Surface morphology of ZnO thin films was observed with an atomic force microscope (AFM) in a dynamic scan mode. Average surface roughness (Ra) was calculated analyzing the AFM results. Sheet resistance of the low-e coatings was measured by a four-probe method to estimate the resistivity of Ag thin films in the low-e coatings.

3. RESULTS AND DISCUSSION

3.1 ZnO single layer

Figure 1 shows the XRD patterns of ZnO thin films deposited in various oxygen gas pressure. It can be seen from Fig. 1 that when the ZnO thin films were deposited in low gas pressure, the well-crystallized and preferentially oriented ZnO thin films were obtained; furthermore, the diffraction peak clearly shifted to low angle. This change in the diffraction angle indicates that the ZnO thin films were compressively distorted with the decrease of the oxygen gas pressure. The relative packing density and surface roughness of

Fig. 1. XRD patterns of ZnO thin films deposited in various oxygen gas pressure (P_{O_2}), where (b) is magnification of (a).

Fig. 2. (a) Relative packing density and (b) surface roughness (Rms) of ZnO thin films deposited in various oxygen gas pressure.

ZnO thin films were estimated from the GIXR results and they are represented as a function of oxygen gas pressure in Fig. 2. It was found from Fig. 2 that the packing density of ZnO thin films systematically increased with decreasing the oxygen gas pressure; moreover, the ZnO deposited in low oxygen gas pressure exhibited smooth surface. The AFM images of the ZnO thin films are demonstrated in Fig. 3. It was confirmed from Fig. 3 that the surface of ZnO thin films became smooth as oxygen gas pressure was decreased. This surface morphology change of ZnO thin films agreed well with the GIXR results. Besides, a clear relationship between the crystal grain size of ZnO thin films and oxygen gas pressure was not confirmed.

Fig. 3. AFM images of ZnO thin films deposited in various oxygen gas pressure of (a) 0.2, (b) 0.5 and (c) 1.0 Pa.

It is known that cathode voltage biased to a sputtering target during sputtering deposition is one of the dominant parameters to determine the thin film properties and microstructures [14], because the kinetic energy of oxygen negative ions recoiled from the sputtering target depends on the cathode voltage. The cathode voltage supplied to the Zn target in the ZnO thin film deposition is plotted in Fig. 4 as a function of oxygen gas pressure. It can be seen in Fig. 4 that the cathode voltage showed almost constant value against oxygen gas pressure, furthermore, a clear relationship was not observed between the cathode voltage and oxygen gas pressure. It can be considered from this result that the microstructure improvement of the ZnO thin films deposited in low oxygen gas pressure is not due to the change in cathode voltage.

Fig. 4. Dependence of cathode voltage on oxygen gas pressure during ZnO sputtering deposition.

Besides, it has been reported that the kinetic energy of the particles, such as oxygen negative ions and sputtered atoms, depends on the collision frequency among the oxygen gas molecules, oxygen negative ions and sputtered atoms [15,16]. In order to clarify the influence of oxygen gas pressure on the collision frequency and kinetic energy of gas particles, the kinetic energy of oxygen negative ion and sputtered Zn atom were estimated using Kevin-Meyer's equation given as follows [15-17]:

$$E_f = (E_i - kT) \exp \left[N \ln \left(\frac{E_f}{E_i} \right) \right] + kT, \quad (2)$$

where E_f is the kinetic energies of the oxygen negative ion and sputtered Zn atom reaching at substrate surface. The initial kinetic energy of those particles are represented by E_i , which are assumed to be 400 eV for oxygen negative ion and 3 eV for sputtered Zn atom. Here, the E_i of oxygen negative ion corresponds to the cathode voltage during ZnO thin film deposition. The terms of k and T are Boltzmann constant and gas temperature, respectively. The collision number is expressed with N , which can be described as follows:

$$N = \left(\frac{dp\sigma}{kT} \right), \quad (3)$$

where d is the distance between the substrate and sputtering target. The terms of p and σ are oxygen gas pressure and collision cross section of oxygen gas,

Fig. 5. (a) Collision number and (b) kinetic energy of oxygen negative ion and (c) collision number and (d) kinetic energy of sputtered Zn atom calculated using Kevin-Meyer's equation.

respectively. The estimated collision number and kinetic energies of oxygen negative ion and sputtered Zn atom are shown as a function of oxygen gas pressure in Fig. 5. Figure 5 indicates that the collision number decreased with the decrease in the oxygen gas pressure, on the other hand, the kinetic energies significantly increased. This theoretical calculation supports that the drastic increase in the kinetic energy of these particles is caused by the decrease of the collision number; in consequence, the microstructure the ZnO thin films deposited in low oxygen gas pressure should be influenced. It can be considered that the oxygen negative ions have enough kinetic energy to impact on the ZnO thin film in low oxygen gas pressure; therefore, oxygen negative ions can cause the atomic peening effect [18], which results in the compressive distortion and high packing density of ZnO thin films. Besides, the oxygen negative ions can be accelerated by cathode voltage with the direction vertical to substrate surface; hence, the ZnO thin films with preferential crystal orientation vertical to substrate surface were grown when they were deposited in low oxygen gas pressure. Furthermore, it can be said that high kinetic energy of sputtered Zn atoms in low oxygen gas pressure can lead

to an increase of migration of Zn atoms on substrate surface during thin film growth; as a result, the ZnO thin films with high packing density and smooth surface can be obtained.

3.2 Double-layered low-e coatings

Figure 6 shows the resistivity change of the Ag thin films used in the double-layered low-e coatings against

Fig. 6. Dependence of resistivity of Ag thin films used in low-e coatings on oxygen gas pressure during ZnO deposition.

Fig. 7. Change in resistivity of Ag thin films used in double-layered low-e coatings as a function of (a) XRD intensity, (b) relative packing density and (c) surface roughness of ZnO under layer.

oxygen gas pressure during the ZnO under layer deposition. It can be seen from Fig. 6 that the resistivity of Ag thin films clearly decreased when the ZnO under layers were deposited under lower oxygen gas pressure. This variation of the resistivity of Ag thin films should be due to the microstructure change of ZnO under layers.

Figure 7 shows the dependence of the Ag thin film resistivity used in the double-layered low-e coating on the microstructure parameter of ZnO under layers, such as the XRD intensity, packing density and surface roughness of ZnO under layers. Figure 7 indicates that the resistivity of Ag thin films decreased when the ZnO under layers exhibited high XRD intensity, high packing density and smooth surface roughness. We have already reported on the basis of the XRD measurement results that the Ag thin films were highly crystallized on ZnO under layers [12]. It can be considered that the heteroepitaxial-like growth of Ag thin films was preferentially promoted when they were deposited on the ZnO thin films with high crystallization, high packing density and smooth surface, in consequence, the resistivity of Ag thin films should decrease.

4. SUMMARY

The microstructures of ZnO thin films were investigated as a function of oxygen gas pressure during deposition. The following results were obtained:

- (1) When low oxygen gas pressure was applied, the ZnO thin films with preferential orientation and compressive distortion were obtained.
- (2) The ZnO thin films deposited in low oxygen gas pressure exhibited high packing density and smooth roughness.

It can be concluded that these microstructure changes of ZnO thin films should come from the effects of oxygen negative ions and sputtered Zn atoms with high kinetic energy during the sputtering deposition; besides, it was found that the kinetic energy of these particles strongly depends on the collision frequency with oxygen gas molecules. Furthermore, the resistivity of double-layered low-e coatings were investigated and it was found that the Ag thin films with low resistivity were obtained using ZnO thin films with preferential orientation of ZnO (002) lattice plane, high packing density and smooth surface.

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